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Palladium Catalyst. III. Reduction of Ketones

BY WALTER H. HARTUNG AND FRANK S. CROSSLEY

The reduction of oximes and nitriles by means of palladium on charcoal to pure primary amines has been described,¹ and the role of hydrogen chloride in the reduction of oximino ketones, *e. g.*, isonitrosopropiophenone, has been studied.² In order to determine more specifically the effect of this hydrogenation procedure on the ketonic group alone, experiments were initiated with propiophenone itself.

expected from propiophenone was the corresponding carbinol, at least as an intermediate. However, the first experiment revealed that hydrogen absorption did not stop when one molar equivalent, necessary for carbinol formation, had been taken up, but continued at an undiminished rate until two equivalents were used. The reduction product was identified as propylbenzene. Further experimentation revealed that

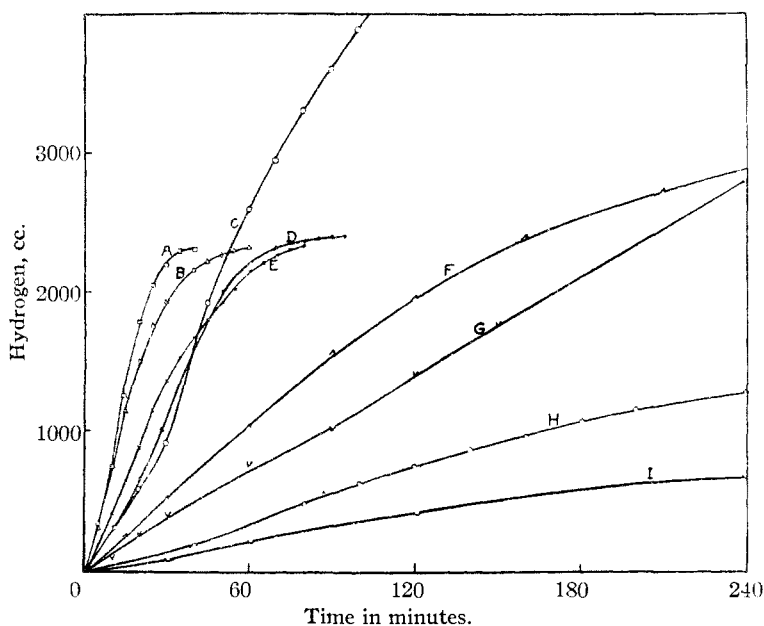


Fig. 1.—Reduction of rates propiophenone and derivatives: A, propiophenone 0.05 mole; B, *m*-propionylphenol 0.05 mole, same catalyst repeated with same amount of ketone reproduced this reduction; C, *p*-propionylanisole 0.10 mole, 4750 ml. H₂ taken up in 160 minutes; D, propionylcatechol 0.045 mole; E, *p*-propionylphenol 0.05 mole, same catalyst repeated with same amount of ketone required 360 minutes; F, *o*-propionylanisole 0.10 mole, 4620 ml. H₂ taken up in 13 hrs., catalyst fortified after 7.5 hrs.; G, *m*-propionylanisole 0.07 mole, 4150 ml. H₂ taken up in 585 minutes; H, propionylresorcinol 0.03 mole, continued at slowly decreasing rate for 120 minutes more (see Table I); I, *o*-propionylphenol 0.10 mole, catalyst fortified after 4 hrs., total time for reduction, 15 hrs.

A considerable degree of parallelism between the activity of palladium and platinum catalysts was anticipated,³ and the reduction product

(1) Hartung *et al.*, THIS JOURNAL, (a) **50**, 3370 (1928); (b) **51**, 2262 (1929); (c) **52**, 3317 (1930); (d) **53**, 1875 (1931); (e) **53**, 4149 (1931).

(2) Hartung, *ibid.*, **53**, 2248 (1931).

(3) *Cf.* Skita and Meyer, *Ber.*, **45**, 3589 (1912); Shriner and Adams, THIS JOURNAL, **46**, 1685 (1924); Füllebin, *Compt. rend.*, **175**, 1077 (1922); **177**, 1118 (1923).

the use of ordinary 95% alcohol instead of absolute alcohol as a solvent had no effect on the extent of the reduction but did decrease the rate; nor did the absence or presence, in varying amounts, of hydrogen chloride alter either the rate or extent of the reduction; also it was found that the catalyst could be used repeatedly, at least as much as six times, without any apparent loss in activity. Every catalyst, similarly prepared and tried, has been found to act in the same manner. In fact, it has since been found that the activity of a catalyst, suspected of being poisoned or otherwise inactivated in other types of hydrogenation, may be conveniently and quickly determined by testing its activity toward propiophenone.

In some instances the reduction was interrupted before the two equivalents of hydrogen were taken up and, from the product, propylbenzene and propiophenone could be isolated; there was no evidence of phenylethylcarbinol. Only in one instance was there even the

suggestion of the formation of the carbinol, and this where the activity of the catalyst appeared to be modified by previous use in connection with a different type of compound.

This reduction reaction has been extended to other aryl alkyl ketones, and the results with various derivatives of propiophenone are given. The effect of structure on the rate of reduction

is shown in Fig. 1, but the product in every instance is the corresponding, substantially pure, derivative of propylbenzene, except, perhaps, in the case of propionylresorcinol.

A catalyst, similarly prepared with platinum, was completely inactive toward propiophenone, although active toward isonitrosopropiophenone. This result is particularly interesting in connection with the recent report of Zelinsky, Packendorff and Leder-Packendorff,⁴ who found it desirable, in the reduction of acetophenone and its derivatives to ethylbenzene, to activate platinized charcoal by the addition of palladium.

Experimental

The reduction procedure and the catalyst have been described.^{1a} The solvent was alcohol, preferably anhydrous. The following ketones were used: propiophenone, *o*- and *p*-hydroxypropiophenone,⁵ propionylresorcinol,⁶ propionylcatechol, *m*-propionylphenol, *o*- and *p*-methoxypropiophenone⁷ and *m*-methoxypropiophenone.⁸ The reduction products are given in Table I.

(4) Zelinsky, Packendorff and Leder-Packendorff, *Ber.*, **66**, 872 (1933).

(5) Miller and Hartung, "Organic Syntheses," Vol. XIII, 1933, p. 90.

(6) Johnson and Lane, *THIS JOURNAL*, **43**, 348 (1921).

(7) Hartung, Munch, Miller and Crossley, *ibid.*, **53**, 4154 (1931).

(8) Cf. Hiers and Hager, "Organic Syntheses," Vol. IX, 1929, p. 13.

TABLE I

Product	Boiling point, uncorr.		Ref.
	°C.	Mm.	
Propylbenzene	163-165	...	9
<i>p</i> -Propylphenol	108	6	10
<i>m</i> -Propylphenol	100-102	6-7	11 ^a
<i>o</i> -Propylphenol	112-115	18-20	12
Propylresorcinol	182-186	5-7	13 ^b
Propylcatechol	136-139	4-5	14 ^c
<i>p</i> -Propylanisole	125	45	15
<i>m</i> -Propylanisole	90-91	5	11
<i>o</i> -Propylanisole	95-98	9	16

^a Aqueous solution gave slight brown color with ferric chloride; alcoholic solution remained colorless.

^b Gave deep color with ferric chloride. Pure alkylresorcinols give practically no color.

^c M. p. ca. 30°; described as melting at 56-60°.¹⁴

Summary

1. It was found that palladium on charcoal quickly and easily reduces propiophenone to propylbenzene. A platinum catalyst similarly prepared was inactive.

2. The substitution of hydroxyl or methoxyl groups in propiophenone influences the rate but not the extent of the reduction.

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(9) Beilstein, 4th ed., Vol. V, p. 390.

(10) Klages, *Ber.*, **32**, 1438 (1899).

(11) Ciamician and Silber, *ibid.*, **23**, 1162 (1890).

(12) Frankland and Turner, *J. Chem. Soc.*, **43**, 357 (1883).

(13) Johnson and Lane, *THIS JOURNAL*, **43**, 348 (1921).

(14) Beilstein, 4th ed., Vol. VI, p. 920.

(15) Beilstein, 4th ed., Vol. VI, p. 500.

(16) Spica, *Gazz. chim. ital.*, **8**, 418 (1878).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Studies in the Chlorophyll Series. XII. The Phaeopurpurins¹

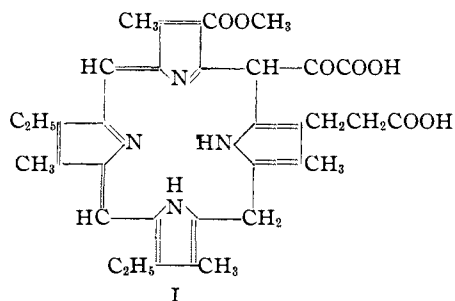
BY EMMA M. DIETZ AND WILLIAM F. ROSS

In previous papers from this Laboratory we have reported the formation of two substances, phaeopurpurin 18 and phaeopurpurin 7² (a monomethyl ester) from the unstable chlorins. The latter compounds are formed by the "phase test hydrolysis" of the phaeophorbides and chlorin *e* trimethyl ester. The structure of phaeopurpurin 7, obtained in this way or by alkaline hydrolysis of dimethyl phaeopurpurin 7 (a trimethyl ester), has been established by a number of transformations as being that of an alpha ketonic acid with the carboxyl group of the pyrrol ring esterified³ (Formula I).

(1) The authors wish to acknowledge the direction and advice of Professor James B. Conant throughout the course of this research.

(2) Paper III, *THIS JOURNAL*, **52**, 3013 (1930).

(3) Paper IV, *ibid.*, **53**, 362 (1931); Paper XI, *ibid.*, **55**, 839 (1933).



We have now been able to obtain further proof of the correctness of this formula since phaeopurpurin 7 can be oxidized to a monomethyl ester of a tribasic acid with loss of carbon dioxide. The parent tribasic acid is chlorin *a* prepared in this Laboratory in our earlier work (Paper III)